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WATER FLUORIDE NUMBER 3

Earl F. McFarren, et al

Environmental Control Administration
Cincinnati, Ohio

1969

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Environmental Control Administration

WATER FLUORIDE NO. 3

STUDY NUMBER 33

ANALYTICAL REFERENCE SERVICE

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service

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WATER FLUORIDE NO. 3

Study Number 33

Report of a Study Conducted by

ANALYTICAL REFERENCE SERVICE

Earl F. McFarren, B.J. Moorman
and J.H. Parker
CINCINNATI TRAINING PROGRAM

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service
Environmental Control Administration
Cincinnati, Ohio 45202
1969

Public Health Service Publication No. 1895

FOREWORD

The Analytical Reference Service (ARS) is conducted by the Cincinnati Training Program of the Environmental Control Administration to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollutional compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the membership, consultants, and the ARS staff. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with copies of the methods to be studied and forms for reporting numerical values, a critique of the procedures, comments or modifications used, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Initially directed toward examination of water, studies now include methods for analysis of air, milk, and food. Some studies are periodically repeated for the advantage of new members, the evaluation of new methods, or the reevaluation of existing methods.

The selection of studies is guided by requests from standard methods committees and the responses to questionnaires periodically circulated among the membership, which now includes 293 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

STUDIES COMPLETED AND REPORTED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. Studies completed in 1957 and 1962. These same metals plus silver. Study completed in 1965. Except for the substitution of magnesium for aluminum, these same metals analyzed by atomic absorption in 1967.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure. Studies completed in 1958 and 1961. Fluoride by ion exchange and fluoride electrode. Study completed in 1968.
Water-Radioactivity	Gross beta activity. Studies completed in 1959 and 1961. Gross beta and strontium-90 activity. Study completed in 1963.
Water-Surfactant	Surfactant in various waters. Studies completed in 1959, 1963, and 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand. Study completed in 1960. Chemical oxygen demand. Study completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium. Study completed in 1962. These same metals plus vanadium. Study completed in 1966.
Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification. Study completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen. Study completed in 1966.

Water-Phenols	Phenol and 2,4-dichlorophenol in water by two specified methods. Study completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods. Study completed in 1967.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats. Study completed in 1958.
Air-Lead	Filter paper tape impregnated with lead. Study completed in 1960.
Air-Particulates	Microscopic identification of some common atmospheric particulates. Study completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method. Study completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water. Study completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT and methoxychlor in water. Study completed in 1968.
Food-Pesticides	DDT in milk. Study completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk. Study completed in 1965.

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PREFACE

The constantly increasing number of communities fluoridating their water supplies has made the measurement of fluoride a routine analysis in many laboratories. Since strict control of the concentration of fluoride is required, and most of the currently used methods of analysis are sensitive to interferences commonly encountered in surface waters, better methods of analysis have been sought. As a result of an evaluation in our laboratory of several new methods for the determination of fluoride that have come into existence in the past few years, it was determined that at least two were worthy of collaborative study: the fluoride electrode and the ion-exchange methods.

The lanthanum alizarin complexone method also was investigated by the Analytical Reference Service (ARS) and found to be useful for high salinity waters but not for ordinary waters because of the long time required for color development and the sensitivity to aluminum interference.

Other analytical procedures, such as the alizarin visual method (Scott-Sanchis), the alizarin photometric method (Megregian-Maier), the eriochrome cyanine R method, and the SPADNS with distillation method had already been evaluated in previous ARS studies (Water Fluoride, March 1958 and Water Fluoride, August 1961), and, hence, it was not felt necessary to reevaluate these procedures.

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ACKNOWLEDGMENTS

Michael J. Taras, Chairman, Joint Editorial Board of Standard Methods for the Examination of Water and Wastewater, made the initial contact and worked out an arrangement with Orion Research, Incorporated whereby they would provide fluoride electrodes and meters on a loan basis to participants who did not own the necessary equipment but wished to participate in the collaborative study.

C. A. Rossiter, General Sales Manager, Orion Research, Incorporated, arranged with their dealer-distributors for the distribution of the electrodes and meters to the participants who indicated a desire to acquire an instrument for the study on a loan basis.

Dr. Martin Frant, Associate Director of Research, Orion Research, Incorporated, Mr. Ervin Bellack, Water Supply and Sea Resources Program, Environmental Control Administration, Bethesda, Maryland, and Mr. Robert Kroner, Division of Pollution Surveillance, Federal Water Pollution Control Administration, Cincinnati, Ohio, were consulted regarding procedures and studies that they had carried out, using the fluoride electrode.

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Reynolds Metals Company, Malvern, Arkansas
Reynolds Metals Company, Massena, New York
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San Jose Health Department, California
Sandia Corporation, Albuquerque, New Mexico
Seattle Water Department, Washington
South Carolina State Board of Health, Columbia
South Dakota State Department of Health, Pierre
Springwells Filtration Plant, Dearborn, Michigan
Stanford Research Institute, Menlo Park, California

Sydney Water Board, Australia
Tennessee Valley Authority, Chattanooga
Texas Agricultural and Mechanical University, College Station
Texas Gulf Sulphur Company, Aurora, North Carolina
Tracerlab/West, Richmond, California
USDI, FWPCA, AWTR Activities, Pomona, California
USDI, FWPCA, Ohio River Basin Project, Evansville, Indiana
USDI, FWPCA, Ohio River Basin Project, Wheeling, West Virginia
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USDI, FWPCA, Technical Advisory and Investigations Branch, Cincinnati, Ohio
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Vermont State Department of Public Health, Burlington
Washington State Department of Public Health, Seattle
Washington State University, Pullman
West Virginia Department of Natural Resources, Charleston
Wisconsin State Laboratory of Hygiene, Madison

ABSTRACT

In this report the results obtained on analysis of three water samples for fluoride by an electrode method, an ion-exchange method and a modified electrode method are compared.

In the analysis of samples containing no interference and of those containing polyphosphates, the electrode method was generally more precise (relative standard deviation 3.6 and 4.8 percent versus 6.0 and 9.6 percent) and more accurate (relative error of 0.7 and 0.2 versus 2.8 and 4.5 percent) than the ion-exchange method. In analyzing a sample containing aluminum and sulfate, however, the modified electrode method (additional citrate added to the sample) gave better results than either the unmodified electrode method or ion-exchange method: a relative standard deviation of 2.9 versus 17.7 and 12.1 percent and a relative error of 4.9 versus 32.0 and 12.8 percent.

It should be stressed that the results obtained by either the modified electrode or the ion-exchange method are acceptable. The simplicity of the operation of the electrode, however, makes the former the method of choice.

WATER FLUORIDE NO. 3

DESIGN OF THE STUDY

Three fluoride samples were prepared to evaluate the electrode (Appendix A) and the ion-exchange (Appendix B) methods. Sample 1 contained a concentration of 0.85 mg of fluoride per liter. Sample 2 contained 0.90 mg of fluoride, 0.50 mg of aluminum, and 200 mg of sulfate per liter. Sample 3 contained 0.75 mg of fluoride, 2.5 mg sodium hexametaphosphate, and 300 mg of alkalinity (added as sodium bicarbonate) per liter.

Aliquots of the solutions were shipped in 1-quart disposable polyethylene containers to 126 participants. Sent with the samples were copies of the methods, report forms, and instructions to do a single analysis of each of the three samples by one or both of the provided methods. The participants were also instructed to note on the report form any procedural modifications that they may have used.

To help obtain the data needed to evaluate the fluoride electrode method, Orion Research, Incorporated, agreed to provide a meter and an electrode to laboratories not having the equipment but wishing to participate. Because of the cost involved, Orion was able to lend only 50 electrodes and meters. These were distributed on a first come, first serve basis to 25 laboratories in the eastern half of the continental United States and 25 in the western part (Montana, Wyoming, Colorado, New Mexico, and west).

TREATMENT OF THE DATA

As the results were received from the participants, the data was reviewed. In the case of a suspected mathematical error, the reporting laboratory was contacted and asked to check its calculations and then to submit a corrected value if an error was found. The data were then grouped and coded according to method and analyzed by a comptuer for normality of distribution. Data that deviated significantly from the normal distribution because of indeterminate errors were rejected, as discussed under "Tests for Normality and Rejection of Outliers" in Appendix F.

After removing the outliers from consideration, the remaining results were used to calculate the statistical measures of precision and accuracy, and the methods were compared by appropriate statistical tests (Appendix G).

To pictorially present the data, bar graphs are included in the text. On these bar graphs rejected values are indicated by broken bars, and numerical values are given for bars that extend beyond the scale of the graph.

DISCUSSION OF THE RESULTS

All the laboratories to which fluoride electrodes were lent also received meters. Another 38 laboratories, which already had electrodes, also used Orion meters. The remaining 32 laboratories that submitted results used other makes: 11 used a Beckman meter, seven a Corning, four a Leeds and Northrup, and 10 used various other kinds.

Initially, the electrode method[1] data was grouped according to meter, fluoride electrode, and reference electrode used by the participant, but the result was so many groups and so few data in some groups that statistical comparisons were not feasible. Furthermore, those groups that could be compared (see Appendix D) had about the same excellent precision and accuracy as did the overall results. Consequently, these variables have been excluded from all subsequent consideration.

Likewise, the data obtained by using either beryllium nitrate, sulfate, or carbonate in the preparation of the eluting reagent for the ion-exchange method[3] gave similar and acceptable results. Hence, these variables also have been excluded from further consideration.

Fifteen other methods or modifications (4 through 18) of either the electrode or ion-exchange method were used by the participants in the analysis of the samples. Most of these were peculiar to so few laboratories that statistical consideration of their data would be of questionable value. These results are individually tabulated in Appendix C and are catalogued as methods 4 through 18 both there and in the reference section of this report.

Thus, only three methods remain to be compared and discussed in this report: the electrode, the ion-exchange, and the modified (by addition of citrate) electrode.

Sample 1: 0.85 mg fluoride per liter (Table 1; Figures 1 and 2)

The results obtained on the analysis of sample 1 by the electrode method[1] (see Table 1) and also by the ion-exchange method[3] were very precise and accurate. Statistically, however the electrode method is both significantly more precise and more accurate than the ion-exchange method.

Sample 2: 0.90 mg fluoride plus 0.50 mg aluminum and 200 mg sulfate per liter (Table 2; Figures 3, 4, and 5)

Relatively poor precision and accuracy were achieved by both the electrode[1] and the ion-exchange[3] methods in the analysis of sample 2, presumably because of the interferences present.

Table 1. SUMMARY OF DATA ON SAMPLE 1
(0.85 mg fluoride per liter)

	Electrode method	Ion-exchange method
Number of results	111	22
Number of outliers	7	3
Mean	0.844	0.874
95% Confidence limits	±0.006	±0.025
Mean error	-0.006	+0.024
Standard deviation	0.030	0.052
Relative error	0.7	2.8
Relative standard deviation	3.6	6.0
95% Tolerance limits	±0.067	±0.145

Sulfate does not interfere, however, in the measurement of fluoride by the electrode method, and the aluminum should have been complexed by the citrate added to the sample in the buffer prior to analysis. Since both significantly more precise and more accurate results were obtained by the modified electrode method[2] than by either of the other two, it appears that an insufficient amount of citrate was specified in the buffer used for the electrode method. In the modified method, 0.5 to 3.0 ml of 1 molar soldium citrate solution was added to the sample prior to buffering, and as a result a relative error of 4.9 percent versus 32.0 percent without added citrate and a relative standard deviation of 2.9 versus 17.7 percent were obtained. None of the 13 results submitted, however, were greater in value than the 0.90 mg fluoride per liter contained in sample 2. This may have been caused by participants using a standard curve, which was constructed with standard solutions not containing the added citrate. The addition of 1 molar citrate to the sample alters the total ionic strength and thereby establishes a significantly different membrane potential in the sample than in the standard containing the same amount of fluoride. In the ARS laboratory, it has been found that increasing the amount of citrate in the TISAB solution from 0.3 g to 12 g per liter overcomes these difficulties and that this amount of citrate will compensate for as much as 2 mg per liter of aluminum.

Theoretically, both aluminum and sulfate interfere in the colorimetric determination of fluoride with the SPADNS reagent used in the ion-exchange method. The prior resin treatment, however, should have removed the sulfate, and the EDTA used in the procedure should have complexed the aluminum. It seems obvious that one or both of the interferences was not entirely eliminated, since in the analysis of sample 2 the relative error was 12.8 percent versus 2.8 percent in

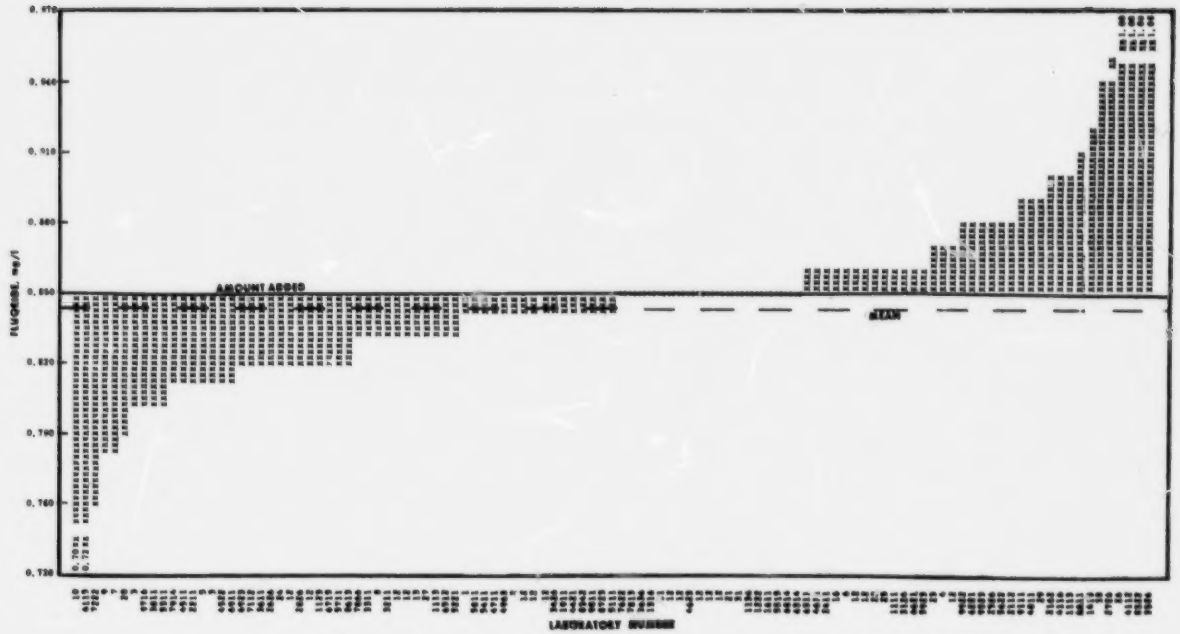

Figure 1. Bar graph for sample 1 by electrode method

the analysis of sample 1, and the relative standard deviation was 12.1 versus 6.0 percent.

It is also conceivable that the participants did not allow for the longer reaction time required with SPADNS by this method when aluminum is present, as this also would account for the consistently low results. Nevertheless, in the analysis of sample 2 by the ion-exchange method, both the precision and accuracy are considered acceptable.

Table 2. SUMMARY OF DATA ON SAMPLE 2
(0.90 mg fluoride per liter, 0.50 mg aluminum per liter, 200 mg sulfate per liter)

	Electrode method	Modified electrode method	Ion-exchange method
Number of results	100	13	22
Number of outliers	0	0	3
Mean	0.612	0.856	0.785
95% Confidence limits	±0.021	±0.015	±0.046
Mean error	-0.288	-0.044	-0.115
Standard deviation	0.108	0.025	0.095
Relative error	32.0	4.9	12.8
Relative standard deviation	17.7	2.9	12.1
95% Tolerance limits	±0.242	±0.077	±0.265

Sample 3: 0.75 mg fluoride plus 2.5 mg of sodium hexametaphosphate and 300 mg of alkalinity (added as sodium bicarbonate) per liter (Table 3; Figures 6 and 7)

Very good precision and accuracy were obtained on analysis of sample 3 by the electrode method[1] (relative error 0.2 percent and relative standard deviation 4.8 percent). The results obtained by the ion-exchange method,[3] although significantly less precise, were not significantly less accurate (see Table 3) than the results for the electrode method.

Since the SPADNS reagent is very sensitive to phosphate, the poorer results may be due to inconsistent removal of phosphate by the resin or inconsistent elution of the fluoride from the resin. In any case, although the electrode results are somewhat better, the ion-exchange results are still very acceptable.

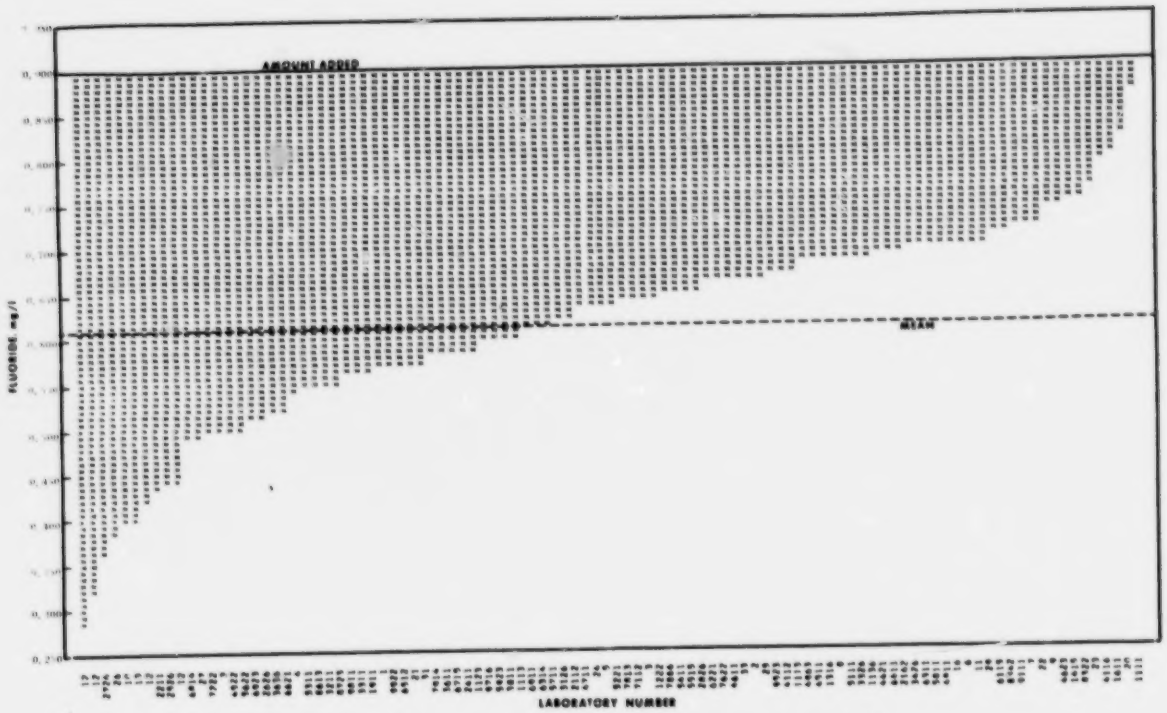

Figure 3. Bar graph for sample 2 by electrode method

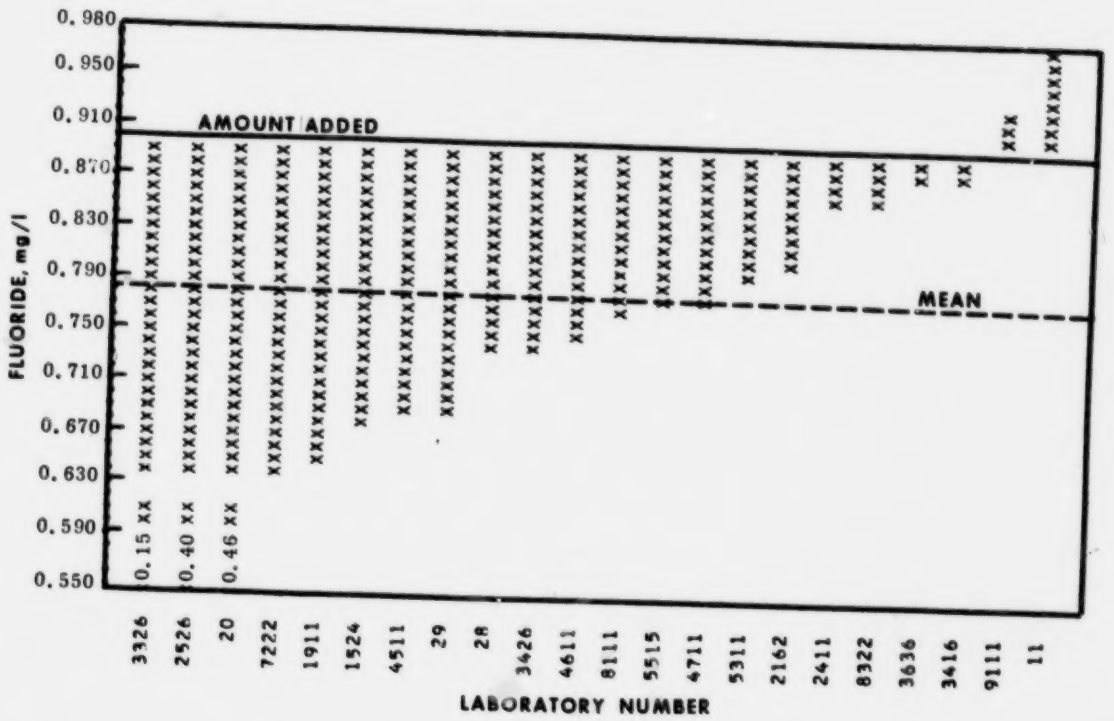

Figure 4. Bar graph for sample 2 by ion-exchange method

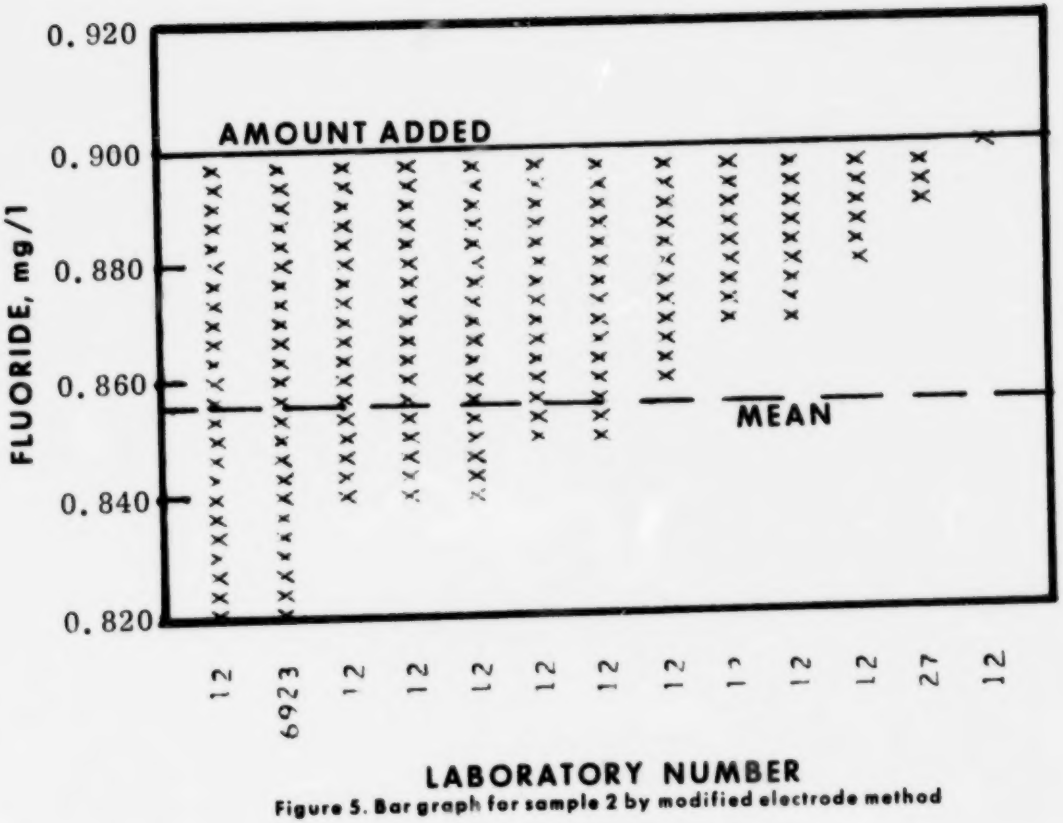

Figure 5. Bar graph for sample 2 by modified electrode method

Table 3. SUMMARY OF DATA ON SAMPLE 3
(0.75 mg fluoride per liter, 2.5 mg polyphosphate per liter, 300 mg alkalinity per liter)

	Electrode method	Ion-exchange method
Number of results	111	22
Number of outliers	4	3
Mean	0.748	0.784
95% Confidence limits	±0.007	±0.036
Mean error	-0.002	+0.034
Standard deviation	0.036	0.075
Relative error	0.2	4.5
Relative standard deviation	4.8	9.6
95% Tolerance limits	±0.079	±0.210

COMMENTS OF THE PARTICIPANTS

ELECTRODE METHOD

"Orion electrode method worked well" is the most representative remark of all the comments made about the method. One participant, however, observed, "The electrodes appeared to work well at first, but soon the time required to reach equilibrium became excessive." By "excessive" he is speaking of 3 to 5 minutes. He continued his remarks by stating that perhaps a wait of 3 minutes to obtain equilibrium by the new black electrode was not too bad," but it means that we could do only 12 to 15 samples per hour by the electrode, whereas we can do 15 to 20 samples in a batch by the SPADNS method in a half hour."

STANDARDS

Many expressed concern over the ambiguity of the instructions for the construction of the standard curve (see Appendix A, Electrode Method, paragraph 5.2). It centers about a factor of 2. Two laboratories suggested corrective changes. One wants the curve constructed by using the true concentrations and, then, applying an appropriate dilution factor. The second wants the wording of the procedure changed to eliminate the ambiguity.

(Editor's comment: It is true that the concentration of 1 ml, 2 ml, etc. of a standard fluoride solution (1 ml = 0.01 mg F^-) when individually diluted to 100 ml is equal to 0.1 mg/l, 0.2 mg/l, etc., respectively, and not 0.2 mg/l, 0.4 mg/l, etc. as stated in the procedure. In the method,

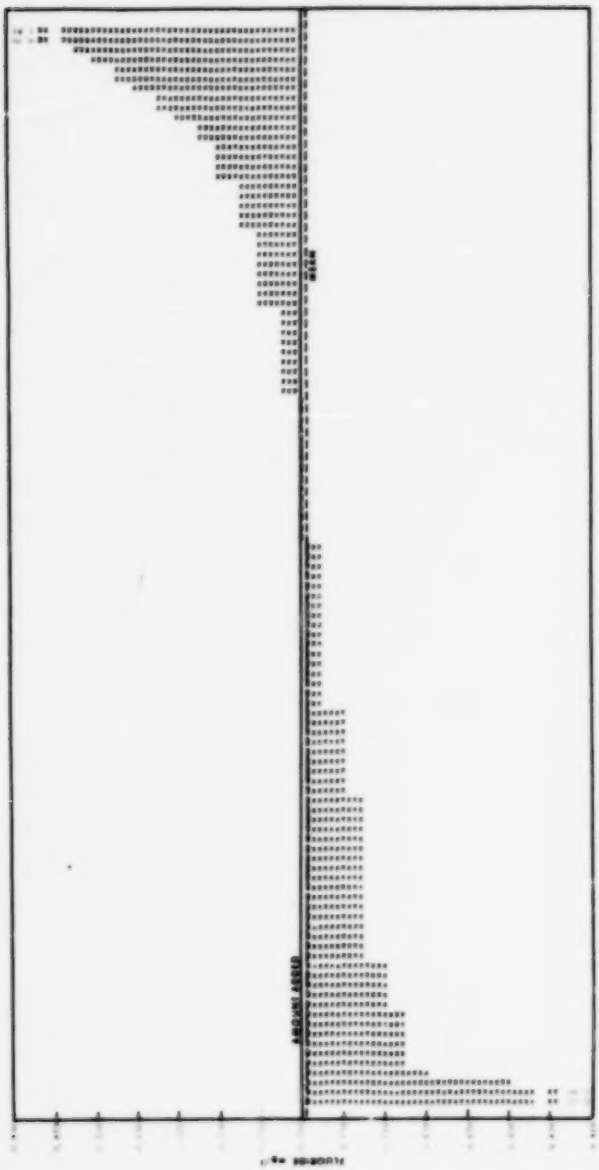

Figure 6. Bar graph for sample 3 by electrode method

Figure 7. Bar graph for sample 3 by ion-exchange method.

however, 50 ml of an unknown sample is diluted to 100 ml with TISAB solution; that is, the original concentration of the sample is cut in half. Therefore, for the convenience of the analyst, doubling the standards' true concentration enables him to read the sample's original concentration directly. Hence, a change in the wording of the procedure from "are equal to 0.00, 0.2, etc." to "are made equivalent to 0.00, 0.2, etc.," is advisable.)

STANDARD CURVE CONSTRUCTION

Two participants mentioned that they modified the procedure for constructing the standard curve. One read and expressed the potential reading as a logarithmic function and plotted it on linear paper. A second participant used an expanded pH scale of 6 to 8 to construct a curve reading directly from 0.1 to 10 mg per liter of fluoride.

ELECTRODE STABILITY

"I was quite impressed with the stability of the instrument. It held its initial calibration for well over 2 hours." A second participant commented, "After the last sample, the 1.00 mg/l F standard was rerun and found to read the same as originally."

CITRATE ADDITION

Many commented that the amount of citrate prescribed in the recipe for the TISAB buffer solution was not sufficient to eliminate the interferences due to aluminum in sample 2. Most suggested increasing the citrate-to-aluminum concentration ratio. One participant did this by diluting one part sample to one part distilled water, and then treating the diluted solution with an equal volume of TISAB buffer solution. Others suggested increasing the amount of citrate. Amounts added to 50 ml of sample 2 ranged from 0.015 g sodium citrate, which is not enough, to 0.9 sodium citrate.

Various addition techniques were used. The citrate was added as part of a 40% formaldehyde, citric acid, hydroxide buffer; as a 1M sodium citrate solution prior to TISAB buffering; and as the solid sodium citrate with and without potassium chloride.

"TISAB" MODIFICATION

One participant suggested a FISAB solution (fluoride ionic strength adjustment buffer). Only one milliliter of this new buffer is used with 50 ml of the sample. It is prepared with 200 g sodium chloride, 15 g citric acid, and 58 g sodium acetate, diluted to 1000 ml after its pH is adjusted to 5.25 with sodium hydroxide or hydrochloric acid.

The advantages claimed are economy and ease of use because of the small volume of buffer and the increased sensitivity since the samples are not substantially diluted.

ALUMINUM INTERFERENCE

Five participants commented upon the peculiar meter response that is characteristic of aluminum's presence in a fluoride sample. The most obvious is that the presence of aluminum increases the time required to reach a stable potential reading. One participant suggested that hours are required; another suggested days. Besides the low values being extensively discussed, the nonreproducibility of the results also received the attention of five laboratories. (Editor's note: The tabulated data in Appendix C demonstrate the erratic results very well.)

Finally, one laboratory attributed to aluminum's presence a nervous-type movement of the meter needle during measurement of the fluoride activity.

ION-EXCHANGE METHOD

According to one participant, "The ion-exchange method didn't work at all!" A second participant commented, "Chemist who used it (ion-exchange method) is mystified by your preference for it." Another complained, ". . . preparation of the resin for the ion-exchange method is rather tedious and time consuming." The expressions "tedious" and 'time-consuming" were often used to describe the method.

ION-EXCHANGE COLUMNS

The ion-exchange columns described in the procedure are difficult to obtain. Three participants commented that they modified chromatographic columns and glass tubing, and substituted these innovations for the commercial column.

SUMMARY AND CONCLUSIONS

In the analysis of sample 1 (no interference) and sample 3, which contains polyphosphate, very excellent accuracy (relative errors of 2.8 and 4.5 percent, respectively) and precision (relative standard deviations of 6.0 and 9.6 percent, respectively) were obtained by the electrode method. In the analysis of sample 2, however, which contained aluminum, very poor precision and accuracy were obtained. When the method was modified by the addition of at least 0.5 ml of 1 molar citrate to the sample berfore adding the buffer, the 0.5 mg per liter of aluminum was complexed, and very satisfactory results were

obtained (relative error 4.9 percent and relative standard deviation 2.9 percent). Presumably, even better accuracy could have been obtained if the citrate had been added to both the standards and the samples. For best results, therefore, it is recommended that the amount of citrate in the "TISAB" solution used in the electrode method be increased from 0.3 to 12.0 g per liter. Under these circumstances, in the ARS laboratory it was found that as much as 2 mg per liter of aluminum could be tolerated.

Of all the electrode combinations possible (Appendix D) the new model fluoride electrode with a sleeve-type reference electrode was recommended (see Electrode Method, Appendix A) and is still the preferred combination. With the sleeve-type reference electrode, equilibrium is established more quickly (1 to 2 minutes versus 3 to 5 minutes with other combinations), and the new model fluoride electrode is of better design: with the new construction there is less possibility of the electrolyte leaking, which eventually renders the electrode inoperative, and less possibility of entrapping air about the solid state (crystal) membrane, which causes erroneous and erratic results.

In the analysis of sample 1 by the ion-exchange method, less precise (relative standard deviation 6.0 percent versus 3.6 percent) and accurate (relative error 2.8 percent versus 0.7 percent) results were obtained than were obtained by the electrode method, but the results are acceptable. Likewise, in the analysis of samples containing sulfate and aluminum interference (sample 2), the ion-exchange procedure is less accurate (relative error 12.8 percent versus 4.9 percent) and precise (relative standard deviation 12.1 percent versus 2.9 percent) than the modified (citrate added) electrode method (see Table 4). Although in the analysis of samples containing polyphosphates (sample 3), the ion-exchange method appears to be less accurate than the electrode method (relative errors of 4.5 and 0.2, respectively), the appropriate statistical test did not indicate a significant difference in accuracy. The ion-exchange method, however, is significantly less precise (relative standard deviation 9.6 percent versus 4.8 percent).

In addition to being generally less precise and accurate, the ion-exchange method also suffers because of the following disadvantages: difficulty in acquiring the required glassware and beryllium compound; too many chemicals and pieces of equipment with which to contend; excessive amount of time consumed. It should be stressed, however, that acceptable results can be obtained with the ion-exchange method, but, because of simplicity and somewhat better precision and accuracy, the modified electrode method is the preferred method of analysis.

Table 4. COMPARISON OF METHODS

Method	Statistical measure	No interference (sample 1)	Aluminum and sulfate (sample 2)	Polyphosphate (sample 3)
Ion-exchange	Relative standard deviation	6.0	12.1	9.6
	Relative error	2.8	12.8	4.5
Electrode	Relative standard deviation	3.6	17.7	4.8
	Relative error	0.7	32.0	0.2
Modified electrode	Relative standard deviation	---	2.9	---
	Relative error	---	4.9	---

REFERENCES

1. Electrode method. Appendix A.

2. Ref. #1, modified by the addition of 0.5 ml to 3.0 ml of 1 M citrate solution to the sample.

3. Ion-exchange method, Appendix B.

4. SPADNS Method for Fluoride. Standard Methods for the Examination of Water and Wastewater. pp. 144-46 with long reaction time or with distillation, pp. 137-38, 12th edition. APHA, AWWA, WPCF. New York, 1965.

5. Alizarin Photometric Method for Fluoride. Standard Methods for the Examination of Water and Wastewater. pp. 142-44. 12th edition. APHA, AWWA, WPCF. New York, 1965 and Alizarin Visual Method for Fluoride. Standard Methods for the Examination of Water and Wastewater. pp. 141-42. 12th edition, APHA, AWWA, WPCF. New York, 1965.

6. Reference 4 modified by using Auto-Analyzer with distillation.

7. Greenhalgh, R., and J. P. Riley. Lanthanum Alizarin Complexone. Anal. Chim. Acta. 25:179-188. 1961.

8. Reference 4 without distillation or long reaction time.

9. Quantitative Colorimetric Determination of Fluoride with AMADAC-F. Standard Operating Procedure. Burdick & Jackson Laboratories. Muskegon, Michigan, 1967.

10. Preliminary Steam Distillation. Standard Methods for the Examination of Water and Wastewater. pp. 138-40. 12th edition. APHA, AWWA, WPCF. New York, 1965, followed by measurement with fluoride electrode, Reference 1.

11. Baumann, E. W. and E. G. Orebaugh. Measurement of Fluoride Concentrations with Specific Ion Electrodes, (unpublished), modified by using 5 percent phosphoric acid.

12. Reference 3 modified by developing color with Eriochrome Cyanine R rather than with SPADNS.

13. Reference 1, modified by substituting 1 ml of Fluoride Ionic Strength Adjustment Buffer (FISAB) containing: 0.200 g NaCl, 0.015 g citric acid, 0.058 g sodium acetate, pH 5.25; for 50 ml of TISAB per 50 ml of sample.

14. Reference 1, modified by the addition of 1.5 g of KCl and 0.1 g sodium citrate to 50 ml of solution.

15. Frazier, R. E. and H. G. Oldfield. Rapid Method for Distilling Fluorides from Water Samples. Public Health Reports, 68:729-731, 1953 and Zirconium-Eriochrome Cyanine Method for Fluoride. ASTM Standards, Part 23 - Industrial Water, Atmospheric Analysis. pp. 210-12. ASTM. Philadelphia, 1964.

16. Reference 1, modified by making all solutions 0.02 M with respect to $NaNO_3$, instead of using the TISAB solution; also, by using a new model fluoride electrode altered for continuous flow analysis.

17. Willard, H. H., and O. B. Winter. Volumetric Method for Determination of Fluorine. Ind. Eng. Chem., Anal. Ed. 5:7-10, 1933.

18. Reference 1, modified by altering the pH of the TISAB solution from between 5.0-5.5 to between 6.2-7.2.

19. Sample Type III-B (Water, Fluoride), Analytical Reference Service, Robert A. Taft Sanitary Engineering Center. Cincinnati, 1961.

APPENDICES

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APPENDIX A.

ELECTRODE METHOD

1. GENERAL DISCUSSION

1.1. Principle: The fluoride ion activity electrode is a specific ion sensor. The electrode is designed to be used with a standard calomel reference electrode and any modern pH meter having an expanded millivolt scale. The key element in the fluoride ion activity electrode is the laser-type, doped, single (LaF_3) crystal across which a potential is established by the presence of fluoride ions. The crystal contacts the sample solution at one face and an internal reference solution at the other. The cell may be represented by Ag|AgCl, Cl^-(0.3), F^-(0.001 M)|LaF_3|test soln|SCE.

The fluoride ion activity electrode can be used to measure the activity or the concentration of fluoride in aqueous samples by use of an appropriate calibration curve. The fluoride activity is dependent, however, upon the total ionic strength of the sample, and the electrode does not respond to fluorides that are bound or complexed. These difficulties are largely overcome by the addition of citrate ions to preferentially complex aluminum and the addition of a solution of high total ionic strength to swamp out variations in sample ionic strength.

1.2. Interference: Polyvalent cations such as Si^{++++}, Al^{+++} and Fe^{+++} will complex fluoride ion. The extent to which complexation takes place depends on the solution pH, and the relative levels of the fluoride and the complexing species. The addition of citrate ion, however, will preferentially complex low concentrations (less than 0.3 mg/l) of aluminum and release the fluoride as the free ion. Likewise, in acid solution, hydrogen ion forms complexes with fluoride ion, but the complexing is negligible if the pH is adjusted to above pH 5. In alkaline solution the hydroxide ion also interferes with the electrode response to fluoride ion whenever the level of hydroxide ion is greater than one-tenth of the level of fluoride ion present. At pH 8 and below, however, the hydroxide concentration is 10^{-6} molar or less, and no interference occurs with any measurable fluoride concentration.

2. APPARATUS

2.1. Expanded scale pH meter or specific ion meter.

2.2. Sleeve-type reference electrode (Orion #90-01-00, Beckman #40463, or Corning #476012). Fiber-tip references are often erratic in very dilute solutions and are not recommended.

2.3. Fluoride electrode (Orion).

2.4. Magnetic stirrer. Teflon-coated stirring bar.

2.5. Stop watch or clock.

3. REAGENTS

3.1. Stock fluoride solution: Dissolve 0.2210 g anhydrous sodium fluoride, NaF, in distilled water, and dilute to 1000 ml; 1.00 ml = 0.100 mg F.

3.2. Standard fluoride solution: Dilute 100 ml stock fluoride solution to 1000 ml with distilled water; 1.00 ml = 0.010 mg F.

3.3. Total ionic strength adjustment buffer (TISAB): Place approximately 500 ml of distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 grams of sodium chloride, and 0.30 grams of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling), insert a calibrated pH electrode and reference electrode into the solution, and slowly add approximately 5M sodium hydroxide (about 150 ml) until the pH is between 5.0 and 5.5. Cool to room temperature. Put into a 1-liter volumetric flask, and add distilled water to the mark.

4. INSTRUMENT CALIBRATION

4.1. No major adjustment of any of the instruments is normally required to use the electrodes in the concentration range 0.2 to 2.0 mg per liter. For those instruments with zero at center scale (e.g. most Beckman or Leeds and Northrop meters), it is convenient to set the instrument by adjusting the calibration control so that the 1.0 mg per liter standard reads at the center zero (100 mv) when the meter is in the expanded scale position. This cannot be done on meters (e.g. Corning Model 12) that do not have a mv calibration control. If using a specific ion meter, follow the directions of the manufacturer in calibrating the instruments.

5. PROCEDURE

5.1. Prepare a series of standards by adding 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 ml of standard fluoride solution (1 ml = 0.01 mg F^-) to a series of 100 ml volumetric flasks. To each flask, add by pipet 50 ml of pH 5.0 to 5.5 TISAB solution, dilute to 100 ml with distilled water, and mix well. These standards are equal to 0.00, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, and 2.0 mg per liter, respectively.

5.2. To a 100 ml volumetric flask, add by pipet 50 ml of sample, dilute to the mark with TISAB, and mix well. The standards and sample should be adjusted to the same temperature; approximately room temperature (25°C ± 2.0) is preferred.

5.3. Transfer each standard and sample to a series of 150 ml beakers. Immerse the electrodes, and measure the developed potential while stirring the test solution on a magnetic stirrer. A caution to observe is that stirring of the solution before immersion of the electrodes may entrap air around the crystal and produce erroneous readings or needle fluctuations. The electrodes must remain in the solution 3 minutes before a final + millivolt reading is taken, and the electrodes should be rinsed with distilled water and blotted dry between each reading.

5.4. When using an expanded scale pH meter, or specific ion meter, it is necessary to frequently recalibrate the electrode. This is done by checking the potential reading 1.0 mg per liter standard, and adjusting the calibration control (if necessary) until the meter reads as before. The calibration should be checked after reading each unknown and also after reading each standard when preparing the standard curve.

5.5. Plot the potential measurement of the fluoride standards against concentration on 2-cycle semilogarithmic graph paper. Plot mg per liter on the logarithmic axis, with the lowest concentration at the bottom of the page. Using the potential measurement for each unknown sample, read the corresponding fluoride concentration off the standard curve.

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APPENDIX B.

ION-EXCHANGE METHOD

1. PRINCIPLE

The adsorption of fluoride on an anion-exchange resin and subsequent stripping by formation of a beryllium-fluoride complex effectively removes substances that interfere in the subsequent spectrophotometric analysis. Distillation of the samples to remove these interferences is thereby eliminated.

2. APPARATUS

2.1. Spectrophotometer, for use at 570 mμ, providing a light path of at least 1 cm.

2.2. Chromatographic columns, 10 mm i.d. by 300 mm, with Squibb separatory funnels and connecting 14/35 standard taper male joints. Corning Glass Works order number X-731864.

3. REAGENTS

3.1. Anionic resin, Dowex 2X-8, 50-100 mesh. Purify by placing 450 grams of the resin in a 1500-ml beaker, wash with two 300-ml portions of 95 percent ethanol, two 300 ml portions of distilled water, five 300 ml portions of 3N hydrochloric acid, and finally with five 300 ml portions of distilled water. Stir in each case for 15 minutes before decanting and adding the second portion. Convert resin to the acetate form by adding three 300-ml portions of 1M sodium acetate solution and stirring for 15 minutes before decanting and adding the next portion. Discard supernatant, prepare a 1:1 slurry of the acetate resin in distilled water, and store in a closed polyethylene container. Used resin may be regenerated and used again by recycling as above by starting with the addition of the 3N hydrochloric acid.

3.2. Ethanol, U.S.P.

3.3. Hydrochloric acid, 3N.

3.4. Sodium acetate, 1N: Dissolve 82.04 g $C_2H_3NaO_2$, and dilute to 1 liter with distilled water.

3.5. Stock Beryllium Solution: Pipet 57 ml of glacial acetic acid into 500 ml of distilled water, dissolve 2.6 grams of reagent grade beryl-

lium carbonate* $(BeO)_5CO_2 \cdot 5H_2O$, and dilute to 1 liter with distilled water.

3.6. Beryllium Eluting Solution: Dilute stock beryllium solution 1 to 10 with distilled water to provide the beryllium eluting solution used to remove the fluoride from the acetate resin.

3.7. Ammonia (ethylene dinitrilo) - tetraacetic acid, 0.13M (NH_4 EDTA): Dissolve 50 g of $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$ in 70 ml of concentrated NH_4OH, and dilute to 1 liter with distilled water.

3.8. Purified white quartz sand, 60 to 120 mesh: Purify the sand by digestion at 100°C for 1 hour with 250 ml of 20 percent sodium hydroxide, discard supernatant, and wash with 250 ml of 1:3 hydrochloric acid solution. Wash in 2-liter flask with distilled water until all traces of chloride are removed.

3.9. Stock fluoride solution: Dissolve 0.2210 g anhydrous fluoride NaF, in distilled water, and dilute to 1000 ml; 1.00 ml = 0.100 mg F.

3.10. Standard fluoride solution: Dilute 100.0 ml stock fluoride solution to 1000 ml with distilled water; 1.00 ml = 0.01 mg F.

3.11. SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt (Eastman No. 7309 or equivalent) in distilled water, and dilute to 500 ml. This solution is stable indefinitely if protected from direct sunlight.

3.12. Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, in about 25 ml distilled water. Add 350 ml conc. HCl, and dilute to 500 ml with distilled water.

3.13. Acid zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent to produce a single reagent, that is stable for at least 2 years.

4. PROCEDURE

4.1. Preparation of columns: While the stirrer is mixing the 1:1 slurry of the acetate resin to keep it in suspension, pipet 25 ml into each column reservoir. After the resin has settled in the column, rinse the remaining resin from the sides of the reservoir. Add purified sand

* No longer stocked by Fisher Scientific Co.; however, their beryllium nitrate, $Be(NO_3)_2 \cdot 3H_2O$ is a satisfactory substitute. Use 9.37 g per liter.

to each column to form a top layer approximately 1 cm high. Wash the reservoirs again with distilled water to remove sand particles from the sides, permitting wash water to drain before addition of sample or standard.

4.2. Preparation of standard curve: Prepare fluoride working solutions of 0.00 mg, 0.02 mg, 0.04 mg, and 0.06 mg per 50 ml by diluting appropriate amounts of fluoride standard solution to 50 ml with distilled water. Pass each through a prepared column, and allow it to drain. Discard the drainage.

4.3. Preparation of samples: Prepare individual columns for each sample, pipet 50 ml or an aliquot diluted to 50 ml into each column, and allow it to drain. (If aluminum is present, see 4.6.) Discard the drainage.

4.4. Washing the columns: Wash the standard and sample columns by adding 100 ml of distilled water to the reservoirs. Allow them to drain. Discard the drainage.

4.5. Elution of fluoride: Remove the absorbed fluoride from the resin by pipetting 100.0 ml of the beryllium eluting solution into the reservoirs. Collect the eluate of each into separate 250-ml erlenmeyer flasks.

4.6. Pretreatment: If aluminum is present in excess of 0.5 mg per liter, add 1 ml of the NH_4EDTA solution, followed by 2 ml of 0.5N NaOH to samples and standards. Mix well prior to passing it through the ion-exchange columns.

4.7. Color development: Pipet 20 ml of mixed SPADNS reagent to each 250 erlenmeyer flask containing eluted standards and samples, and mix well. Adjust the standards and samples to within ±2°C of each other if necessary. Read the standards and samples in 1-cm cells after adjusting the spectrophotometer slit so that a reading of 0.500 on the absorbance scale is obtained on the 0.90 standard with the use of a wave length of 570. Prepare a standard curve by plotting mg fluoride versus absorbance, and read the concentration of the samples off the standard curve. If aluminum was present in the samples and NH_4EDTA was added for complete complexation of the aluminum fluoride, then allow a 30-minute waiting period after adding the SPADNS reagent before reading in the spectrophotometer.

5. CALCULATION

$$\text{mg/l F} = \frac{A \times 1000}{\text{ml of sample}}$$

where A = mg F determined spectrophotometrically.

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APPENDIX C.

TABULATION OF RESULTS

Table C-1. Sample 1. Fluoride (0.85 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.84	1	12	0.86	1
2	0.84	1	12	0.82	1
3	0.80	1	12	0.87	1
3	0.81	1	12	0.82	1
4	0.87	1	12	0.84	1
5	0.81	1	13	0.83	1
6	0.86	1	16	0.86	1
7	0.78	1	17	0.89	18
8	0.83	1	18	0.76	16
9	0.78	1	20	0.44	3
10	0.70	1	20	0.79	1
11	0.85	1	20	0.84	7
11	0.88	3	21	0.85	1
11	0.73	9	22	0.86	1
12	0.84	1	23	0.87	1
12	0.84	1	24	0.82	1
12	0.83	1	25	1.28	17
12	0.85	1	25	0.86	1
12	0.85	1	26	1.00	1
12	0.85	1	27	0.88	2
12	0.85	1	27	0.83	1
12	0.85	1	28	0.86	3
12	0.83	1	29	0.89	1
12	0.86	1	29	0.86	3

(Table C-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
31	0.85	1	2526	0.88	1
33	0.94	1	2926	1.00	3
1111	0.86	1	2626	0.79	11
1113	0.83	1	2626	0.82	1
1113	0.90	1	2726	0.95	1
1123	0.80	4	2726	1.00	5
1123	0.82	1	2826	0.82	1
1136	0.85	1	3126	0.86	1
1222	0.85	1	3211	0.83	1
1314	0.87	4	3311	0.83	1
1316	0.85	1	3311	0.83	8
1415	0.92	1	3326	1.06	1
1415	0.86	7	3326	0.77	3
1524	1.20	3	3416	0.88	3
1611	0.85	1	3426	0.86	3
1911	0.87	3	3426	0.84	1
1911	0.86	8	3611	0.72	15
1911	0.[illegible]	1	3611	0.82	1
2112	0.[illegible]	1	3636	0.84	3
2162	0.90	1	3636	0.85	1
2162	0.95	3	3731	0.84	5
2211	0.81	1	3811	0.80	1
2411	0.86	3	4112	1.00	1
2411	0.86	1	4116	0.90	1

(Table C-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4116	0.78	14	5622	0.88	1
4212	0.77	8	5711	0.82	1
4421	0.84	1	5811	0.84	1
4421	0.87	9	5923	0.86	1
4511	0.85	3	6115	0.72	1
4511	0.81	1	6221	0.88	1
4511	0.87	10	6311	0.86	1
4522	0.81	1	6314	0.85	1
4611	0.90	3	6411	0.91	1
4611	0.86	1	6512	0.83	1
4623	0.85	1	6512	0.80	5
4711	0.84	1	6621	0.86	1
4711	0.95	3	6715	0.82	1
4811	0.89	1	6814	0.84	13
4963	0.84	1	6814	0.85	1
5111	0.84	1	6911	0.82	6
5111	0.80	5	6911	0.81	1
5221	0.83	1	6923	0.82	1
5221	0.83	4	6923	0.82	2
5311	0.80	1	7112	0.82	1
5311	0.80	3	7222	0.76	1
5411	0.84	1	7222	0.60	3
5515	0.88	3	7622	0.85	1
5515	0.85	1	7813	0.82	6

(Table C-1 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7813	0.85	1	8723	0.84	1
7866	0.83	1	9111	0.89	1
7866	0.55	12	9111	0.86	5
7914	0.81	1	9111	0.88	3
8111	0.83	3	9523	0.88	1
8322	0.88	3	9716	0.80	1
8322	1.00	1	9811	0.84	1
8342	0.84	1	9922	0.88	1
8613	0.82	1			

Table C-2. Sample 2, Fluoride (0.90 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.57	1	12	0.87	2
2	0.66	1	12	0.88	2
3	0.64	1	12	0.90	2
3	0.50	1	12	0.44	1
4	0.54	1	13	0.40	1
5	0.63	1	16	0.70	1
6	0.70	1	17	0.86	18
7	0.72	1	18	0.00	16
8	0.68	1	20	0.00	7
9	0.74	1	20	0.46	3
10	0.40	1	20	0.82	1
11	0.70	1	21	0.57	1
11	0.98	3	22	0.72	1
12	0.32	1	23	0.76	1
12	0.28	1	24	0.63	1
12	0.42	1	25	1.14	17
12	0.82	2	25	0.66	1
12	0.84	2	26	0.38	1
12	0.84	2	27	0.89	2
12	0.84	2	27	0.49	1
12	0.85	2	28	0.74	3
12	0.85	2	29	0.70	1
12	0.86	2	29	0.69	3
12	0.87	2	31	0.57	1

(Table C-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
33	0.66	1	2526	0.40	3
1111	0.87	1	2626	0.84	11
1113	0.67	1	2626	0.51	1
1113	0.60	1	2726	0.50	5
1123	0.58	1	2726	0.36	1
1123	0.90	4	2826	0.65	1
1136	0.68	1	3126	0.62	1
1222	0.64	1	3211	0.55	1
1314	0.92	4	3311	0.56	1
1316	0.68	1	3311	0.62	8
1415	0.39	7	3326	0.68	1
1415	0.75	1	3326	0.15	3
1524	0.68	3	3416	0.88	3
1611	0.80	1	3426	0.74	3
1911	0.56	1	3426	0.70	1
1911	0.65	3	3611	0.78	15
1911	0.52	8	3611	0.58	1
2112	0.62	1	3636	0.52	1
2162	0.81	3	3636	0.88	3
2162	0.69	1	3731	0.48	5
2211	0.43	1	3811	0.60	1
2411	0.86	3	4112	0.67	1
2411	0.58	1	4116	0.79	1
2526	0.44	1	4116	0.91	14

(Table C-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4212	0.77	8	5811	0.70	1
4421	0.69	1	5923	0.60	1
4511	0.69	3	6115	0.71	1
4511	0.68	1	6221	0.66	1
4511	0.93	10	6311	0.70	1
4522	0.50	1	6314	0.61	1
4611	0.75	3	6411	0.69	1
4611	0.66	1	6512	0.60	5
4623	0.74	1	6512	0.57	1
4711	0.78	3	6621	0.52	1
4711	0.63	1	6715	0.58	1
4811	0.70	1	6814	0.25	13
4963	0.68	1	6814	0.49	1
5111	0.68	1	6911	0.87	6
5111	0.90	5	6911	0.61	1
5221	0.94	4	6923	0.82	2
5221	0.63	1	6923	0.51	1
5311	0.80	3	7112	0.64	1
5311	0.55	1	7222	0.50	1
5411	0.65	1	7222	0.64	3
5515	0.78	3	7622	0.66	1
5515	0.65	1	7813	0.96	6
5622	0.50	1	7813	0.64	1
5711	0.61	1	7866	0.65	1

(Table C-2 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7866	0.62	12	9111	0.90	5
7914	0.58	1	9111	0.93	3
8111	0.77	3	9111	0.72	1
8322	0.75	1	9523	0.67	1
8322	0.86	3	9716	0.60	1
8342	0.71	1	9811	0.56	1
8613	0.55	1	9922	0.57	1
8723	0.55	1			

Table C-3. Sample 3, Fluoride (0.75 mg/liter)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
1	0.74	1	12	0.77	1
2	0.78	1	12	0.74	1
3	0.72	1	12	0.78	1
3	0.72	1	12	0.74	1
4	0.77	1	12	0.74	1
5	0.76	1	13	0.73	1
6	0.76	1	16	0.72	1
7	0.70	1	17	0.80	18
8	0.75	1	18	1.01	16
9	0.71	1	20	0.00	3
10	0.60	1	20	0.85	1
11	0.65	1	20	0.68	7
11	0.68	3	21	0.76	1
11	0.86	9	22	0.76	1
12	0.74	1	23	0.71	1
12	0.72	1	24	0.74	1
12	0.75	1	25	1.10	17
12	0.75	1	25	0.77	1
12	0.75	1	26	0.78	1
12	0.75	1	27	0.79	2
12	0.73	1	27	0.72	1
12	0.72	1	28	0.79	3
12	0.76	1	29	0.82	3
12	0.74	1	29	0.86	1

(Table C-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
31	0.75	1	2526	0.90	3
33	0.84	1	2526	0.78	1
1111	0.77	1	2626	0.72	11
1113	0.78	1	2626	0.73	1
1113	0.72	1	2726	0.50	1
1123	0.85	4	2726	0.48	5
1123	0.72	1	2826	0.73	1
1136	0.76	1	3126	0.76	1
1222	0.75	1	3211	0.70	1
1314	0.92	4	3311	0.99	8
1316	1.01	1	3311	0.79	1
1415	0.80	1	3326	0.82	1
1415	0.71	7	3326	0.91	3
1524	0.52	3	3416	0.68	3
1611	0.73	1	3426	0.73	3
1911	0.74	1	3426	0.74	1
1911	0.96	8	3611	0.68	15
1911	0.80	3	3611	0.72	1
2112	0.77	1	3636	0.76	1
2162	0.81	1	3636	0.74	3
2162	0.81	3	3731	0.77	5
2211	0.71	1	3811	0.72	1
2411	0.77	3	4112	0.83	1
2411	0.75	1	4116	0.84	1

(Table C-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
4116	0.96	14	5622	0.79	1
4212	0.72	8	5711	0.70	1
4421	0.72	9	5811	0.73	1
4421	0.75	1	5923	0.75	1
4511	0.72	1	6115	0.70	1
4511	0.71	3	6221	0.79	1
4511	0.80	10	6311	0.77	1
4522	0.72	1	6314	0.72	1
4611	0.75	3	6411	0.82	1
4611	0.74	1	6512	0.80	5
4623	0.75	1	6512	0.74	1
4711	0.74	1	6621	0.76	1
4711	0.95	3	6715	0.73	1
4811	0.77	1	6814	0.90	13
4963	0.74	1	6814	0.77	1
5111	0.75	1	6911	0.73	6
5111	0.80	5	6911	0.71	1
5221	0.94	4	6923	0.73	1
5221	0.75	1	6923	0.73	2
5311	0.72	3	7112	0.72	1
5311	0.71	1	7222	0.70	1
5411	0.72	1	7222	0.50	3
5515	0.74	1	7622	0.74	1
5515	0.80	3	7813	0.78	6

(Table C-3 continued)

LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
7813	0.75	1	8723	0.74	1
7866	0.74	1	9111	0.80	1
7866	0.50	12	9111	0.80	5
7914	0.73	1	9111	0.83	3
8111	0.73	3	9523	0.79	1
8322	0.90	1	9716	0.70	1
8322	0.77	3	9811	0.72	1
8342	0.75	1	9922	0.69	1
8613	0.72	1			

APPENDIX D.

RESULTS SUMMARIZED ACCORDING TO METHOD VARIATION USED

Table D-1. Sample 1 (0.85 mg fluoride per liter)

Method variation	Number of results	Number of outliers	Mean	95% Confidence limits	Mean error	Standard deviation	Relative error	Relative standard deviation	95% Tolerance limits
Electrode combinations:									
New[a] and sleeve reference	73	4	0.841	±0.006	-0.009	0.026	1.0	3.0	±0.059
New and std. reference[b]	12	0	0.845	±0.045	-0.006	0.071	0.7	8.4	±0.225
Old[c] and sleeve reference	9	0	0.861	±0.021	+0.011	0.027	1.3	3.1	±0.096
Old and std. reference[b]	12	1	0.848	±0.027	-0.002	0.043	0.3	5.1	±0.136
Overall	111	7	0.844	±0.006	-0.006	0.030	0.7	3.6	±0.067
Ion-exchange elutents:									
Ion-exchange using $Be(NO_3)_2$	15	3	0.877	±0.032	+0.027	0.058	3.2	6.6	±0.171
Ion-exchange using $(BeO)_5CO_2$	3	0	0.853	±0.052	+0.003	0.021	0.4	2.4	±0.206
Ion-exchange using $BeSO_4$	1	0	0.880	------	------	-----	---	---	------
Overall	22	3	0.874	±0.025	+0.024	0.033	2.8	6.0	±0.145

[a] New model fluoride electrode (black body).

[b] Standard reference electrode (ceramic or fiber tip).

[c] Old model fluoride electrode (white body).

Table D-2. Sample 2 (0.90 mg fluoride, 0.50 mg aluminum, and 200 mg sulfate per liter)

Method variation	Number of results	Number of outliers	Mean	95% Confidence limits	Mean error	Standard deviation	Relative error	Relative standard deviation	95% Tolerance limits
Electrode combinations:									
New[a] and sleeve reference	66	0	0.594	±0.027	-0.306	0.111	34.0	18.6	±0.256
New and std. reference[b]	12	0	0.668	±0.075	-0.232	0.118	25.7	17.6	±0.373
Old[c] and sleeve reference	9	0	0.654	±0.057	-0.246	0.074	27.3	11.3	±0.260
Old and std. reference[b]	12	1	0.643	±0.038	-0.257	0.059	28.5	9.2	±0.188
Overall	100	0	0.612	±0.021	-0.288	0.108	32.0	17.7	±0.242
Modified electrode	13	0	0.856	±0.015	-0.044	0.025	4.9	2.9	±0.077
Ion-exchange elutants:									
Ion-exchange using $Be(NO_3)_2$	15	3	0.791	±0.054	-0.109	0.098	12.1	12.3	±0.288
Ion-exchange using $(BeO)_5CO_2$	3	0	0.720	±0.155	-0.180	0.062	20.0	8.7	±0.619
Ion-exchange using $BeSO_4$	1	0	0.680	------	------	-----	----	----	------
Overall	22	3	0.785	±0.046	-0.115	0.095	12.8	12.1	±0.265

[a] New Model fluoride electrode (black body).

[b] Standard reference electrode (ceramic or fiber tip).

[c] Old model fluoride electrode (white body).

Table D-3. Sample 3 (0.75 mg fluoride, 2.5 mg sodium hexametaphosphate, and 300 mg alkalinity per liter)

Method Variation	Number of results	Number of outliers	Mean	95% Confidence limits	Mean error	Standard deviation	Relative error	Relative standard deviation	95% Tolerance limits
Electrode combinations:									
New[a] and sleeve reference	74	3	0.747	±0.008	-0.006	0.030	0.8	4.0	±0.068
New and std. reference[b]	11	1	0.765	±0.035	+0.015	0.052	1.9	6.9	±0.171
Old[c] and sleeve reference	9	0	0.746	±0.032	-0.004	0.041	0.6	5.5	±0.145
Old and std. reference[b]	12	1	0.751	±0.022	+0.001	0.035	0.1	4.7	±0.112
Overall	111	4	0.748	±0.007	-0.002	0.036	0.2	4.8	±0.079
Ion-exchange elutants:									
Ion-exchange using $Be(NO_3)_2$	15	3	0.803	±0.043	+0.047	0.077	6.2	9.6	±0.227
Ion-exchange using $(BeO)_5CO_2$	3	0	0.753	±0.100	+0.003	0.040	0.4	5.4	±0.401
Ion-exchange using $BeSO_4$	1	0	0.880	------	------	-----	---	---	------
Overall	22	3	0.784	±0.036	+0.034	0.075	4.5	9.6	±0.210

[a] New model fluoride electrode (black body).

[b] Standard reference electrode (ceramic or fiber tip).

[c] Old model fluoride electrode (white body)

APPENDIX E.

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniformity of understanding.

Arithmetic mean — The sum of the sample results divided by the number of results in the sample. Let X_i ($i = 1, 2, \ldots, n$) denote the i^{th} result in a sample of n results. The arithmetic mean denoted $\overline{X}$ is given by $\overline{X} = \sum_{i=1}^{n} \frac{X_i}{n}$.

Median — Halfway point in the results when they have been arranged in order of magnitude (the middle result of an odd number of results, or the average of the middle two for an even number).

Accuracy — The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).

Measures of accuracy — Measures that relate to the difference between the mean of the results and the true value when the latter is known or assumed. The following measures apply:

Mean error – The average difference with regard to sign between the results and the true value. Equivalently, the difference between the mean of the results and the true value (T. V.).

$$\text{Mean error} = \overline{X} - \text{T. V.}$$

Relative error – The absolute value of the mean error expressed as a percentage of the true value.

$$\text{Relative error} = \frac{|\overline{X} - \text{T. V.}|}{\text{T. V.}} \times 100$$

Precision — The reproducibility of sample results or the degree of agreement among the results.

Measures of precision

Measures of the variation among the sample results themselves, i.e., the spread or dispersion of the results without regard to the true value. The following measures apply:

Sample variance – Sum of squared deviations of the sample results from their mean divided by one less than the number of results in the sample. The sample variance denoted s^2 is given by

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}$$

where n is the number of results.

Sample standard deviation – Square root of the sample variance.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \bar{X})^2}{n - 1}}$$

Relative standard deviation (coefficient of variation) – Sample standard deviation expressed as a percentage of the mean.

$$\text{Rel. Std. Dev.} = \frac{s}{\bar{X}} \times 100$$

Range – The difference between the largest and smallest results in the sample.

Confidence limits – Limits within which the true mean, μ, of the population (the theoretically infinite number of possible replications of the analysis) will lie with probability equal to $1 - \alpha$, where α is the probability that the limits do not contain the true mean. The upper and lower $1 - \alpha$ confidence limits are given by

$$\text{Confidence limits} = \bar{X} \pm t_{\alpha/2} s/\sqrt{n}$$

where $\overline{X}$ and s are the sample mean and standard deviation, $t_{\alpha/2}$ is the upper $\alpha/2$ point of "Student's" t-distribution, and n is the number of results in the sample used to compute $\overline{X}$.

Tolerance limits – Limits within which one can state with probability γ that at least a proportion P of the entire population will lie. The upper and low tolerance limits are given by,

$$\text{Tolerance limits} = \overline{X} \pm Ks.$$

where $K^{(1)}$ is the factor for two-sided tolerance limits for normal populations. The value of K depends upon the chosen values of γ and P.

REFERENCES

1. Natrella, M. G. Experimental Statistics. National Bureau of Standards. 1963. p. T-10.

APPENDIX F.

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness-of-fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution.[1]

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it with the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness-of-fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon.[2] Briefly, this test involves computing a ratio that compares the distance of the suspected value being tested from its neighbors with the range of all, or most all, of the observations (depending on the total number of suspected values in the sample). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted.

3. If the distribution is designated as normal, and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[3] This method employs the statistic $\frac{\overline{X} - X_o}{s}$ where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the

farthest value from the mean), and s is the sample standard deviation. This statistic is compared to a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and the subsequent test for rejection of outliers are applied to the observed data in two ways: first, to each method for a given substance at a given level of concentration; then to a given substance at a given level of concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1. This cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection, and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made, and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of

observations is no longer greater than 30; in which case, method 2 is used for testing for rejection of any remaining suspected outliers.

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1. Siegel, S. Nonparametric Statistics for the Behavioral Sciences. McGraw-Hill Book Co., Inc. New York, N.Y., 1956, pp. 47-51.

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3. Personal communication. J. Santner. Mathematical Sciences. Office of the Director. Robert A. Taft Sanitary Engineering Center. 1966.

APPENDIX G.

COMPARISON OF METHODS FOR STATISTICALLY SIGNIFICANT DIFFERENCES IN PRECISION AND ACCURACY

The methods are compared in two ways with respect to precision and accuracy. In the first case, two methods are compared at a given level of concentration with respect to precision and to accuracy. The unknown variances, σ_1^2 and σ_2^2 (estimated by the sample variances, s_1^2 and s_2^2), of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The unknown means, μ_1 and μ_2 (estimated by the sample means, $\overline{X}_1$ and $\overline{X}_2$), of the two methods then are compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the result of the F-test. These two tests of hypotheses will produce one of the following results.

Outcome 1: $\sigma_1^2 = \sigma_2^2$, $\mu_1 = \mu_2$

Outcome 2: $\sigma_1^2 = \sigma_2^2$, $\mu_1 \neq \mu_2$

Outcome 3: $\sigma_1^2 \neq \sigma_2^2$, $\mu_1 = \mu_2$

Outcome 4: $\sigma_1^2 \neq \sigma_2^2$, $\mu_1 \neq \mu_2$

In outcome 1, we conclude that the sample results do not indicate that a significant difference in either precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no indication of a significant difference in precision between the two methods, but there is a signifcant difference in the accuracy of the two methods: specifically, the method whose sample mean is closer to the true value is deemed the more accurate. In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the two methods, but the method with the smaller sample variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller sample variance is the more precise, and the method whose sample mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and accuracy. Bartlett's Test[3] is used first to test the hypothesis of equality of the unknown variances, σ_i^2, of the methods in order to compare the precision of the methods. If we conclude that the precision is the same, the Analysis of Variance[4] is then used to test whether a significant difference exists among the means, μ_i, in order to compare the accuracy of the methods. If there is a significant difference among the means. Duncan's Multiple Range Test[5, 6] is used to determine by which method the means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-way Analysis of Variance by Ranks[7] is used to determine whether a significant difference exists among the means in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes for the above tests of hypotheses.

Outcome 1: all σ_i^2 are equal, all μ_i are equal

Outcome 2: all σ_i^2 are equal, not all μ_i are equal

Outcome 3: not all σ_i^2 are equal, all μ_i are equal

Outcome 4: not all σ_i^2 are equal, not all μ_i are equal

In outcome 1, we conclude that the sample results do not indicate a significant difference in either the precision or the accuracy of the methods.

In outcome 2, we conclude that there is no indication of a significant difference in the precision of the methods; however, at least one method does differ significantly from the rest with respect to accuracy, and Duncan's Multiple Range Test indicates which methods differ. For example, in comparing four methods, we might conclude $\mu_1 = \mu_2$ and $\mu_3 = \mu_4$, but μ_1 and μ_2 differ significantly from μ_3 and μ_4; or we might conclude that $\mu_1 = \mu_2 = \mu_3$ but μ_4 differs significantly from μ_1, μ_2, and μ_3.

In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the methods, but at least one method differs significantly from the rest with respect to precision.

In outcome 4, we conclude that the methods differ significantly with respect to both precision and accuracy.

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7. Siegel, Sidney. Nonparametric Statistics. McGraw-Hill. 1956. pp. 184-94.

APPENDIX H.

ANALYTICAL REFERENCE SERVICE MEMBERSHIP

STATE AGENCIES

Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
Arizona State Department of Health, Phoenix
Arkansas Pollution Control Commission, Little Rock
Arkansas State Department of Health, Little Rock
California Department of Water Resources, Sacramento
California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation Laboratory, Berkeley
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Delaware Water and Air Resources Commission, Dover
District of Columbia Department of Public Health, Washington, D.C.
Florida Department of Agriculture, Tallahassee
Florida State Board of Health, Jacksonville
Florida State Board of Health, Pensacola
Florida State Board of Health, Winter Haven
Hawaii State Department of Health, Laboratories Branch, Honolulu
Hawaii State Department of Health, Occupational and Radiological Health Section, Honolulu
Idaho Department of Health, Boise
Illinois Department of Public Health, Springfield
Illinois State Water Survey, Champaign
Illinois State Water Survey, Peoria
Indiana State Board of Health, Indianapolis
Iowa State Hygienic Laboratory, Des Moines
Iowa State Hygienic Laboratory, Iowa City
Kentucky State Department of Health, Division of Laboratory Services, Frankfort
Kentucky State Department of Health, Radiological Health Program, Frankfort
Lawrence Experiment Station, Massachusetts
Louisiana State Department of Health, New Orleans
Los Angeles County Flood Control District, California
Maryland State Department of Health, Bureau of Environmental Chemistry, Baltimore
Maryland State Department of Health, Bureau of Laboratories, Baltimore
Maryland State Department of Water Resources, Annapolis
Massachusetts Department of Public Health, Amherst

Massachusetts Department of Public Health, Boston
Michigan Department of Conservation, Lansing
Michigan Department of Public Health, Lansing
Minnesota Department of Agriculture, St. Paul
Minnesota Department of Health, Minneapolis
Missouri Department of Health, Jefferson City
Montana Bureau of Mines and Geology, Butte
Montana Health Department, Helena
Nebraska State Department of Health, Lincoln
Nevada State Department of Health and Welfare, Las Vegas
Nevada State Department of Health, Reno
New Hampshire State Department of Health, Concord
New Hampshire Water Supply and Pollution Control Commission, Concord
New Jersey State Department of Health, Trenton
New Mexico Department of Public Health, Sante Fe
New York State Conservation Department, Avon
New York State Conservation Department, Ronkonkoma
New York State Department of Health, Division of Air Resources, Albany
New York State Department of Health, Division of Laboratories and Research, Albany
New York State Department of Health, Syracuse
New York State Department of Labor, New York City
North Carolina Department of Water and Air Resources, Raleigh
North Dakota State Department of Health, Bismarck
North Jersey District Water Supply Commission, Wanaque
Ohio Department of Agriculture, Reynoldsburg
Ohio State Department of Health, Columbus
Oklahoma State Health Department, Oklahoma City
Oregon State Board of Health, Portland
Pennsylvania Department of Agriculture, Harrisburg
Pennsylvania Department of Health, Division of Air Pollution Control, Harrisburg
Pennsylvania Department of Health, Water Quality Section, Harrisburg
Puerto Rico Institute of Health Laboratories, Hato Rey
Puerto Rico Aqueduct and Sewer Authority, San Juan
Rhode Island State Department of Health, Providence
South Carolina Pollution Control Authority, Columbia
South Dakota Department of Health, Pierre
Tennessee Department of Public Health, Nashville
Tennessee Stream Pollution Control Authority, Nashville
Texas State Department of Health, Austin
Utah State Department of Health, Salt Lake City
Vermont State Department of Health, Barre
Vermont State Department of Health, Burlington
Virginia State Department of Health, Bureau of Industrial Hygiene, Richmond
Virginia State Department of Health, Bureau of Laboratories, Richmond
Virginia State Water Control Board, Richmond

Washington State Department of Health, Seattle
Washington State Food and Drug Laboratory, Seattle
West Virginia Department of Natural Resources, Charleston
Wisconsin Department of Agriculture, Madison

MUNICIPAL AGENCIES

Albuquerque Department of Environmental Health, Air Management Division, New Mexico
Albuquerque Department of Environmental Health, Food and Institutional Division, New Mexico
Baltimore City Health Department, Maryland
Bay Area Air Pollution Control District, San Francisco, California
Beaumont Health Department, Texas
Central Water Filtration Plant, Chicago, Illinois
City of Amarillo, Water Reclamation Department, Texas
City of Charlotte, Water Department, North Carolina
City of Cincinnati, Division of Water Pollution Control, Ohio
City of Durham, Department of Water Resources, North Carolina
City of Erie, Bureau of Water, Pennsylvania
City of Long Beach, Water Department, California
City of Miami, Alexander Orr, Jr. Water Treatment Plant, Florida
City of Newburgh, Water Department, New York
City of New York, Food and Drug Laboratory, New York
City of Niagara Falls, Division of Water Laboratories, New York
City of Philadelphia, Office of the Medical Examiner, Pennsylvania
City of San Jose, Health Department, California
City of Seattle, Water Department, Washington
City of Toledo, Division of Pollution Control, Ohio
City of Yonkers, Bureau of Water, New York
County of Fresno, Department of Public Health, California
County of Los Angeles, Air Pollution Control District, California
Denver Board of Water Commissioners, Colorado
Department of Air Pollution Control, Chicago, Illinois
Department of Public Health, Environmental Health Laboratory, Philadelphia, Pennsylvania
Department of Public Health, Public Health Laboratory, Philadelphia Pennsylvania
Department of Public Works and Utilities, Flint, Michigan
Department of Service and Buildings, Dayton, Ohio
Department of Water and Power, Los Angeles, California
East Bay Municipal Utility District, Oakland, California
Easterly Pollution Control Center, Cleveland, Ohio
Erie County Health Laboratory, Buffalo, New York
Houston City Health Department, Texas
Los Angeles Department of Public Works, Playa Del Rey, California
Louisville Water Company, Kentucky

Metropolitan St. Louis Sewer District, Missouri
Metropolitan Sanitary District of Greater Chicago, Illinois
Metropolitan Utilities District, Omaha, Nebraska
Metropolitan Water District of Southern California, La Verne
Minneapolis Water Department, Minnesota
Monroe County Health Department, Rochester, New York
Nassau County Department of Health, Hempstead, New York
Nassau County Department of Health, Mineola, New York
New York City Department of Air Pollution Control, New York
New York City Health Department, New York
Orange County Air Pollution Control District, Anaheim, California
Philadelphia Water Department, Pennsylvania
Philadelphia Water Department, Belmont Laboratory, Pennsylvania
Philadelphia Water Department, Torresdale Laboratory, Pennsylvania
Riverside County Air Pollution Control District, California
St. Louis Public Health Laboratories, Missouri
Salem and Beverly Water Supply Board, Beverly, Massachusetts
San Diego County Department of Public Health, California

FEDERAL AGENCIES

Brookhaven National Laboratory, Upton, Long Island, New York
DHEW, PHS, Bureau of Community Environmental Management, Cincinnati, Ohio
DHEW, PHS, Bureau of Water Hygiene, Bethesda, Maryland
DHEW, PHS, National Air Pollution Control Administration, Washington, D.C.
DHEW, PHS, Northeast Marine Health Sciences Laboratory, Narragansett, Rhode Island
DHEW, PHS, Northeastern Radiological Health Laboratory, Winchester, Massachusetts
DHEW, PHS, Southwestern Radiological Health Laboratory, Las Vegas, Nevada
Fourth U.S. Army Medical Laboratory, Fort Sam Houston, Texas
Regional Environmental Health Laboratory (LSGHM), McClellan AFB, California
Regional Environmental Health Laboratory (SGHK), Kelly AFB, Texas
Reynolds Electrical and Engineering Company, inc., Las Vegas, Nevada
San Francisco Bay Naval Shipyard, Vallejo, California
Sixth U.S. Army Medical Laboratory, Sausalito, California
Tennessee Valley Authority, Chattanooga
Tennessee Valley Authority, Muscle Shoals, Alabama
U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland
USDA, Soils Laboratory, Beltsville, Maryland
USDI, FWPCA, AWTR Research Activities, Pomona, California
USDI, FWPCA, Alaska Water Laboratory, College
USDI, FWPCA, Analytical Quality Control, Cincinnati, Ohio
USDI, FWPCA, Chemistry and Physics, Cincinnati, Ohio

USDI, FWPCA, Chicago Program Office, Illinois
USDI, FWPCA, North Atlantic Water Quality Management Office, Edison, New Jersey
USDI, FWPCA, Ohio River Basin Project, Evansville, Indiana
USDI, FWPCA, Ohio River Basin Project, Wheeling, West Virginia
USDI, FWPCA, Robert S. Kerr Water Research Center, Ada, Oklahoma
USDI, FWPCA, Technical Advisory and Investigations Branch, Cincinnati, Ohio
USDI, Fish-Pesticide Research Laboratory, Columbia, Missouri
USDI, Geological Survey, Columbus, Ohio
USDI, Geological Survey, Denver, Colorado
USDI, Geological Survey, Harrisburg, Pennsylvania
USDI, Geological Survey, Little Rock, Arkansas
USDI, Geological Survey, Menlo Park, California
Walter Reed Army Medical Center, Washington, D.C.

FOREIGN AGENCIES

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Ciudad Universitaria, Mexico
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Department of Health Services and Hospital Insurance, Vancouver, B.C., Canada
Department of Municipal Laboratories, Hamilton, Ontario, Canada
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Department of National Health and Welfare, Public Health Engineering Division, Ottawa, Ontario, Canada
Department of National Health and Welfare, Public Health Engineering Division, Vancouver, B.C., Canada
Deparlment of Public Health, Sydney, Australia
Institute of Environmental Sanitation, First Section, Taipei, Taiwan, China
Institute of Environmental Sanitation, Division of Quality and Pollution Control, Taipei, Taiwan, China
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University of Leeds, England
Water Commission, Jamaica, West Indies
Water Research Association, Marlow, Buckinghamshire, England

UNIVERSITIES

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Louisiana State University, Baton Rouge
Medical College of South Carolina, Charleston
New Mexico Institute of Mining and Technology, Socorro
New York University Medical Center, New York
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Oak Ridge Institute of Nuclear Studies, Tennessee
Rensselaer Polytechnic Institute, Troy, New York
Rutgers University, New Brunswick, New Jersey
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University of California, Industrial Hygiene Engineering, Berkeley
University of California, Richmond
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University of Kansas, Lawrence
University of Minnesota, Minneapolis
University of North Carolina, Chapel Hill
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University of Vermont, Burlington
University of Wisconsin, Madison
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Washington State University, College of Eng. Research Division, Pullman
Wayne State University, Detroit, Michigan

INDUSTRIES

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